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(12) **UK Patent Application** (19) **GB** (11) **2 188 936** (13) **A**

(43) Application published 14 Oct 1987

(21) Application No 8704914

(22) Date of filing 3 Mar 1987

(30) Priority data

(31) 61/047424
61/142871

(32) 6 Mar 1986
20 Jun 1986

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(51) INT CL⁴

C08G 69/32 69/46 69/48 73/22

(52) Domestic classification (Edition I):

C3R 22D1B2 22D1BX 22D2BX 22N1A 22N1B 22NX 22PX
22T2 7N5A 7PX J SM

(56) Documents cited

None

(58) Field of search

C3R
Selected US specifications from IPC sub-class C08G

(54) **Aromatic polyamides and polybenzoxazoles having diphenylhexafluoropropane units**

(57) An aromatic polyamide, which is high in heat resistance and is soluble in various organic solvents, is obtained by reacting 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane with an aromatic dicarboxylic acid, an aromatic dicarboxylic acid dihalide or an aromatic dicarboxylic acid diester. By a dehydrating and cyclizing reaction the aromatic polyamide can easily be converted into a polybenzoxazole, which is soluble in various organic solvents.

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SPECIFICATION

Aromatic polyamides and polybenzoxazoles having diphenylhexafluoropropane units

5 This invention relates to a group of novel aromatic polyamides having diphenylhexafluoropropane derivative units and a method of preparing the same, and also to a group of aromatic polybenzoxazoles derived from the novel polyamides. 5

Some aromatic polyamides are known as high-strength and heat resistant resins. However, known aromatic polyamide resins are inconvenient for shaping because they lack moldability and also because they are soluble only in limited and special solvents such as strong mineral acids 10 which are corrosive and offer many problems to the practice of spinning or solution casting operations. 10

Some aromatic polybenzoxazoles, such as ones described in Macromol. Chem., Vol. 83 (1965), 167, are excellent in mechanical properties such as tensile strength, flexural strength and impact resistance, heat resistance represented by heat distortion temperature and thermal decomposition temperature, electric properties such as arc resistance and dielectric loss, flame resistance and dimensional stability. However, known aromatic polybenzoxazoles can hardly be used as industrial resins because they are not melt moldable and not soluble in practicable solvents. JP 42-19272 proposes to obtain a polybenzoxazole in a desired form by first casting 20 a solution of a polyamide into the desired form and then converting the polyamide into polybenzoxazole. However, this method is not suited to practical applications because of problems related to the limited solvents for aromatic polyamides. 20

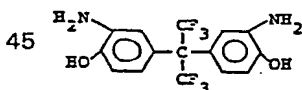
Even though a polymer possesses attractive properties the polymer is of little value as an industrial plastic material unless it has good moldability and/or good solubility in a solvent low in price and convenient for industrial handling. There is little expectation that aromatic polyamides and polybenzoxazoles will be afforded with melt moldability in view of their high melting or softening temperatures. Therefore, solubilities in commonplace solvents become a matter of primary concern. In general, it is effective in improving moldability or solubilities of a polymer to provide some disorder in the molecular structure by introducing a bulky substituent or by 25 copolymerization. However, it is often that such modification of a polymer is accompanied by degradation of heat resistance and possibly some other characteristics of the original polymer. 25

It is an object of the present invention to provide novel aromatic polyamides which are soluble in various organic solvents and possess excellent heat resistance and good mechanical properties. 30

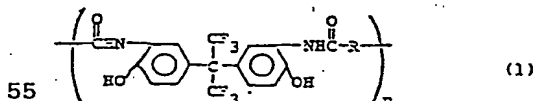
35 It is another object of the invention to provide a method of preparing aromatic polyamides according to the invention. 35

It is still another object of the invention to provide novel polybenzoxazoles, which are derived from aromatic polyamides according to the invention and are soluble in various organic solvents.

We have accomplished the above objects by discovering that a group of aromatic polyamides 40 derived from 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane, viz. a compound of the following formula, are readily soluble in various organic solvents and that a group of polybenzoxazoles derived from these aromatic polyamides are also soluble in various organic solvents. 40

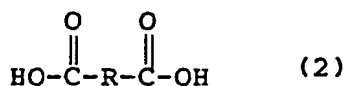


More definitely, this invention provides aromatic polyamides represented by the general formula 50 (1): 50

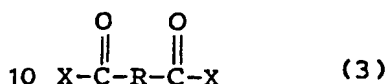


wherein R is a divalent aromatic group, and n is an integer from 1 to 200.

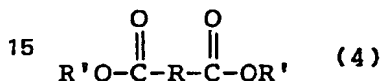
According to the invention an aromatic polyamide represented by the general formula (1) is prepared by reacting 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane with a dicarboxylic acid 60 represented by the general formula (2), a dicarboxylic acid dihalide represented by the general formula (3) or a dicarboxylic acid diester represented by the general formula (4): 60



5 wherein R is a divalent aromatic group;



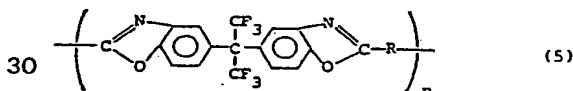
10 wherein R is a divalent aromatic group, and X is a halogen atom;



15 wherein R is a divalent aromatic group, and R' is an alkyl group or a phenyl group.

Aromatic polyamides according to the invention are readily soluble in various and common-
place organic solvents and, therefore, can easily be formed into various shapes from solutions.
20 Besides, these polyamides are excellent in heat resistance and have good mechanical properties.
Accordingly these polyamides are of value as industrial materials. Furthermore, these polyamides
can easily be converted into corresponding polybenzoxazoles, which are soluble in various
organic solvents, by a cyclizing reaction.

25 Using aromatic polyamides represented by the general formula (1), the present invention
provides polybenzoxazoles represented by the general formula (5):



30 wherein R is a divalent aromatic group, and n is an integer from 1 to 200.

These polybenzoxazoles are also soluble in various and commonplace organic solvents and,
35 therefore, can easily be formed into various shapes from solutions. Besides, these polybenzoxa-
zoles are excellent in heat resistance and mechanical properties. Accordingly these polybenzoxa-
zoles are of value as industrial materials.

In preparing an aromatic polyamide according to the invention from 2,2-bis(3-amino-4-hydroxy-
phenyl)hexafluoropropane (will be appreciated to BAHPH-HFP) by reaction with an aromatic dicar-
boxylic acid; any of known dicarboxylic acids represented by the general formula (2) can be
40 employed. The following are examples of dicarboxylic acids favorable in the practice of the
present invention: isophthalic acid, terephthalic acid, 4-4'-biphenyldicarboxylic acid, biphenylether-
4,4'-dicarboxylic acid, benzophenone-4,4'-dicarboxylic acid, benzosulfone-4,4'-dicarboxylic acid,
2,6-naphthalene-dicarboxylic acid, diphenylmethane-4,4'-dicarboxylic acid, 4,4'-isopropylidenedi-
45 phenyl-1,1'-dicarboxylic acid and 4,4'-hexafluoroisopropylidenediphenyl-1,1'-dicarboxylic acid.

Alternatively it is possible, and is rather convenient, to use a dicarboxylic acid dihalide which
may be any of known compounds represented by the general formula (3). Preferable examples
are dichlorides of the above named ten kinds of dicarboxylic acids.

Still alternatively it is possible to use a dicarboxylic acid diester which may be any of known
50 compounds represented by the general formula (4). Preferable examples are diphenyl esters of
the above named ten kinds of dicarboxylic acids.

It is optional to use a mixture of two or more kinds of dicarboxylic acids, or dicarboxylic acid
dihalides or dicarboxylic acid diesters to thereby obtain a copolymer as an aromatic polyamide
according to the invention.

55 In the case of reacting BAHPH-HFP with a dicarboxylic acid represented by the general formula
(2), the reaction is carried out in a suitable organic solvent such as, for example, N,N-dimethyl-
formamide, N,N-dimethylacetamide or N-methyl-2-pyrrolidone at a temperature ranging from room
temperature to the boiling point of the employed solvent. When a dicarboxylic acid dihalide
represented by the general formula (3) is used instead of the acid the reaction is carried out also
60 in a similar organic solvent, and in this case a suitable reaction temperature is in the range from
about -10°C to about 50°C. A similar organic solvent is used also in the case of reacting
BAHPH-HFP with a dicarboxylic acid diester represented by the general formula (4), and in this
case a suitable reaction temperature is in the range from about 50°C to about 300°C.

A polybenzoxazole according to the invention, represented by the general formula (5), is
65 obtained by subjecting a polyamide according to the invention to a dehydrating and cyclizing

reaction. This reaction itself is well known. In general this reaction is accomplished by heating the polyamide for a sufficient period of time at a temperature in the range from about 100°C to about 500°C. It is optional to heat the polyamide in the presence of a dehydrating agent such as, for example, polyphosphoric acid with a view to accomplishing the dehydrating and cyclizing reaction at a relatively low temperature. Also it is optional to carry out the reaction under reduced pressure in view of the possibility of accomplishing the reaction at a relatively low temperature.

Another method of preparing a polybenzoxazole according to the invention is reacting BAHPH-HFP with an aromatic dicarboxylic acid represented by the general formula (2) in polyphosphoric acid. The reaction is carried out at 10–250°C for tens of minutes to several hours. This reaction directly gives a polybenzoxazole.

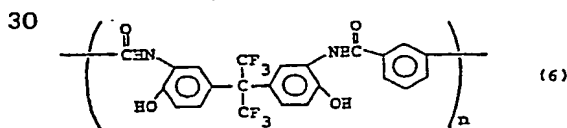
EXAMPLE 1

In a 50 ml three-necked flask having a nitrogen gas inlet, 0.915 g of BAHPH-HFP was dissolved in 5 ml of dimethylacetamide. The solution was freeze-dried by using a bath of dry ice and acetone, and then 0.508 g of isophthalic acid dichloride was put into the flask. After that the bath was changed to an ice bath, and gentle stirring was commenced to cause the freeze-dried solution to gradually melt. The stirring was continued for 5 hr while maintaining a nitrogen gas atmosphere in the flask. As the result a polymer was obtained.

By infrared absorption spectrum analysis the polymer exhibited absorption bands at 1650 cm⁻¹ and 1600 cm⁻¹ which are characteristic of acid amides. Elementary analysis of this polymer gave the following result.

Calculated (%) : C 55.66, H 2.84, N 5.64
Found (%) : C 55.46, H 2.61, N 5.78

Therefore, the obtained polymer was confirmed to be a polyamide represented by the following formula (6).



In sulfuric acid the intrinsic viscosity η_{inh} of this polyamide was 0.08 dL/g at 30°C. This polyamide was soluble in, for example, dimethylformamide, pyridine, 1-methyl-2-pyrrolidone, dimethyl sulfoxide, tetrahydrofuran and acetone.

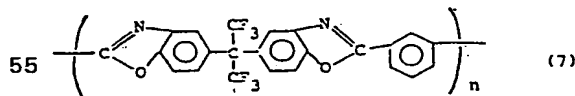
EXAMPLE 2

The polyamide prepared in Example 1 was placed in a glass tube and was heated at 250°C for 20 hr while the pressure in the tube was kept reduced to 1 mmHg or below.

By infrared absorption spectrum analysis after the above heat treatment, the polymer exhibited an absorption band at 1620 cm⁻¹ characteristic of oxazole. Elementary analysis of the heat-treated polymer gave the following result.

Calculated (%) : C 60.01, H 2.19, N 6.08
Found (%) : C 60.13, H 2.26, N 6.31

Therefore, the heat-treated polymer was confirmed to be a polybenzoxazole represented by the following formula (7).



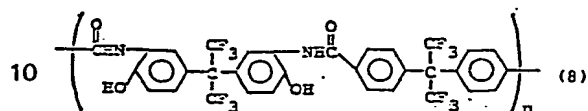
EXAMPLE 3

By the same method as in Example 1, BAHPH-HFP was reacted with 2,2-bis(4-chlorocarbonyl phenyl) hexafluoropropane to obtain a polymer.

By infrared absorption spectrum analysis the polymer exhibited absorptions at 1650 cm⁻¹ and 1600 cm⁻¹. Elementary analysis of this polymer gave the following result.

Calculated (%) : C 53.20, H 2.51, N 3.88
 Found (%) : C 53.17, H 2.34, N 3.91

5 Therefore, the obtained polymer was confirmed to be a polyamide represented by the following formula (8). 5



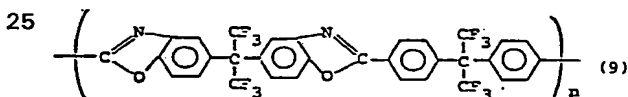
EXAMPLE 4

15 In a glass tube the polyamide prepared in Example 3 was heated at 250°C for 30 hr while the pressure in the tube was kept reduced to 1 mmHg or below. 15

The heat-treated polymer exhibited an infrared absorption at 1620 cm⁻¹, and elementary analysis of this polymer gave the following result.

20 Calculated (%) : C 55.99, H 2.06, N 4.66
 Found (%) : C 55.70, H 2.04, N 4.98 20

Therefore, the heat-treated polymer was confirmed to be a polybenzoxazole represented by the following formula (9).



30 Heat resistance of this polybenzoxazole was examined by thermogravimetric analysis. In air the polymer began to decompose at about 415°C and exhibited 10% loss of weight at 520°C. 30

This polybenzoxazole was soluble in, for example, o-chlorophenol, pyridine, 1-methyl-2-pyrrolidone and dimethylacetamide.

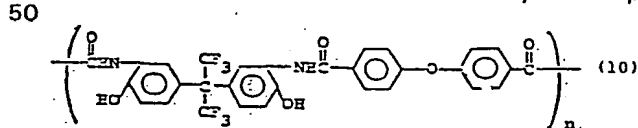
35 EXAMPLE 5 35

In a 100 ml flask connected with a nitrogen gas source and with a reflux condenser, a mixture of 1.830 g (5 millimol) of BAHPPH-HFP, 1.290 g (5 millimol) of 4,4'-oxydibenzoic acid, 10 ml of N-methylpyrrolidone, 2.5 ml of pyridine, 3.1 g (10 millimol) of triphenyl phosphite and 0.5 g of lithium chloride was heated to 100°C in a nitrogen gas atmosphere and was stirred for 6 hr 40 under the same condition. After that the reaction liquid was slowly poured into a large quantity of water to precipitate a white polymer. 40

The obtained polymer exhibited infrared absorptions at 1650 cm⁻¹ and 1600 cm⁻¹, and elementary analysis of this polymer gave the following result.

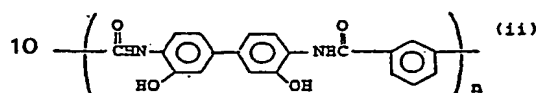
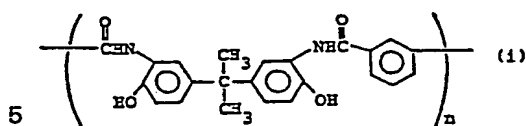
45 Calculated (%) : C 59.19, H 3.08, N 4.76
 Found (%) : C 59.09, H 3.13, N 4.85 45

Therefore, this polymer was confirmed to be a polyamide represented by the following formula (10). In sulfuric acid the intrinsic viscosity of this polyamide was 0.1 dL/g at 30°C. 50



55 COMPARATIVE EXAMPLE 55

For comparison with the polyamides (6), (8) and (10) of Examples 1, 3 and 5, two kinds of known polyamides represented by the following formulas (i) and (ii) were prepared each by a known method.



The polyamide (i) was prepared by reaction of 2,2-bis(3-amino-4-hydroxyphenyl)propane with isophthalic acid-chloride in dimethylacetamide. The polyamide (ii) was prepared by reaction of 4,4'-diamino-3,3'-dihydroxybiphenyl with isophthalic acid chloride in dimethylacetamide.

Solubilities of the novel polyamides (6), (8) and (10) and the known polyamids (i) and (ii) in several kinds of organic solvents were found to be as shown in the following table, wherein the evaluation marks A to D indicate the following results, respectively.

- 20 A: rapidly dissolved.
B: dissolved.
C: partially dissolved.
D: insoluble.
- 20

25

Solvent	Polyamide				
	(6)	(8)	(10)	(i)	(ii)
pyridine	A	A	A	A	D
dimethylformamide	A	A	A	C	D
35 N-methylpyrrolidone	A	A	A	A	A
methanol	C	C	B	D	D
acetone	A	A	A	C	D
40 methyl ethyl ketone	C	C	B	C	D
ethyl acetate	C	C	B	D	D
tetrahydrofuran	A	A	A	C	D

45

EXAMPLE 6

This example relates to preparation of a polybenzoxazole according to the invention by a single-stage process.

In a 100-ml three-necked flask connected with a nitrogen gas source and with a reflux condenser, a mixture of 1.83 g of BAHPH-HFP, 0.83 g of isophthalic acid and 60 g of 116% polyphosphoric acid was subjected to reaction at 200°C for 4 hr in a nitrogen gas atmosphere with continuous stirring. After that the reaction liquid was poured into a large quantity of water to precipitate a polymer. The polymer was washed with a dilute aqueous solution of sodium carbonate and then dried.

The obtained polymer exhibited infrared absorption at 1620 cm⁻¹ characteristic of oxazoles, and elementary analysis of this polymer gave the following result.

60 Calculated (%) : C 60.01, H 2.19, N 6.08
Found (%) : C 59.78, H 2.20, N 6.15

60

Therefore, the obtained polymer was confirmed to be the polybenzoxazole represented by the formula (7) shown in example 2.

EXAMPLE 7

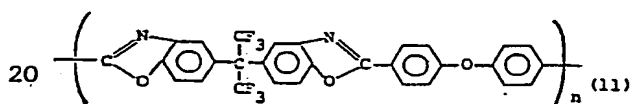
This example too relates to preparation of a polybenzoxazole according to the invention by a single-stage process.

Using the same apparatus as in Example 6, a mixture of 1.83 g of BAHPPH-HFP, 1.29 g of 4,4'-diphenylether dicarboxylic acid and 60 g of 116% polyphosphoric acid was subjected to reaction at 200°C for 4 hr in a nitrogen gas atmosphere with continuous stirring. After that the reaction liquid was poured into a large quantity of water to precipitate a polymer, which was washed and dried in the same manner as in Example 6.

The obtained polymer exhibited infrared absorption at 1620 cm⁻¹, and elementary analysis of this polymer gave the following result.

Calculated (%) : C 63.05, H 2.55, N 8.69
Found (%) : C 62.88, H 2.56, N 8.96

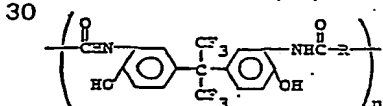
Therefore, this polymer was confirmed to be a polybenzoxazole represented by the following formula (11).



In sulfuric acid the intrinsic viscosity η_{inh} of this polybenzoxazole was 0.08 dL/g at 30°C. Heat resistance of this polymer was examined by thermogravimetric analysis. In air the polymer began to decompose at about 420°C and exhibited 10% loss of weight at 353°C. This polybenzoxazole was soluble in, for example, o-chlorophenol, pyridine and 1-methyl-2-pyrrolidone.

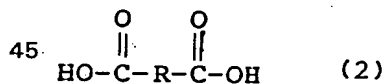
CLAIMS

1. An aromatic polyamide represented by the general formula (1):

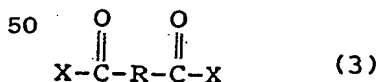


wherein R is a divalent aromatic group, and n is an integer from 1 to 200.

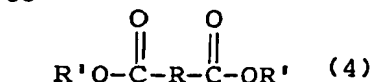
2. An aromatic polyamide according to Claim 1, wherein said R is -C₆H₄-.
3. An aromatic polyamide according to Claim 1, wherein said R is -C₆H₄-C(CF₃)₂-C₆H₄-.
4. An aromatic polyamide according to Claim 1, wherein said R is -C₆H₄-O-C₆H₄-CO-.
5. A method of preparing an aromatic polyamide, comprising the step of reacting 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane with an aromatic dicarboxylic compound selected from dicarboxylic acids represented by the general formula (2), dicarboxylic acid dihalides represented by the general formula (3) and dicarboxylic acid diesters represented by the general formula (4):



wherein R is a divalent aromatic group,



wherein R is a divalent aromatic group, and X is a halogen atom,



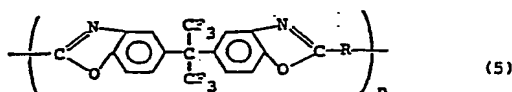
wherein R is a divalent aromatic group, and R' is an alkyl group or a phenyl group.

6. A method according to Claim 5, wherein said aromatic dicarboxylic compound is a dicarboxylic acid selected from isophthalic acid, terephthalic acid, 4,4'-biphenyldicarboxylic acid, biphenylether-4,4'-dicarboxylic acid, benzophenone-4,4'-dicarboxylic acid, benzosulfone-4,4'-dicarboxylic acid, 2,6-naphthalene-dicarboxylic acid, diphenylmethane-4,4'-dicarboxylic acid, 4,4'-isopropylidenediphenyl-1,1'-dicarboxylic acid and 4,4'-hexafluoroisopropylidenediphenyl-1,1'-dicarboxylic acid.

7. A method according to Claim 5, wherein said aromatic dicarboxylic compound is a dicarboxylic acid dichloride selected from isophthalic acid dichloride, terephthalic acid dichloride, 4,4'-bisphenyldicarboxylic acid dichloride, biphenylether-4,4'-dicarboxylic acid dichloride, benzophenone-4,4'-dicarboxylic acid dichloride, benzosulfone-4,4'-dicarboxylic acid dichloride, 2,6-naphthalene-dicarboxylic acid dichloride, diphenylmethane-4,4'-dicarboxylic acid dichloride, 4,4'-isopropylidenediphenyl-1,1'-dicarboxylic acid dichloride and 4,4'-hexafluoroisopropylidenediphenyl-1,1'-dicarboxylic acid dichloride.

8. A method according to Claim 5, wherein said aromatic dicarboxylic compound is a dicarboxylic acid diester selected from diphenyl isophthalate, diphenyl terephthalate, diphenyl 4,4'-biphenyldicarboxylate, diphenyl biphenylether-4,4'-dicarboxylate, diphenyl benzosulfone-4,4'-dicarboxylate, diphenyl 2,6-naphthalenedicarboxylate, diphenyl diphenylmethane-4,4'-dicarboxylate, diphenyl 4,4'-isopropylidene diphenyl-1,1'-dicarboxylate and diphenyl 4,4'-hexafluoroisopropylidene-diphenyl-1,1'-dicarboxylate.

9. A polybenzoxazole represented by the general formula (5):



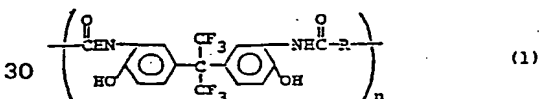
wherein R is a divalent aromatic group, and n is an integer from 1 to 200.

10. A polybenzoxazole according to Claim 9, wherein said R is $-\text{C}_6\text{H}_4-$.

11. A polybenzoxazole according to Claim 9, wherein said R is $-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-$.

12. A polybenzoxazole according to Claim 9, wherein said R is $-\text{C}_6\text{H}_4-\text{C}(\text{CF}_3)_2-\text{C}_6\text{H}_4-$.

13. A method of preparing a polybenzoxazole, comprising the step of subjecting an aromatic polyamide represented by the general formula (1) to dehydrating and cyclizing reaction:



wherein R is a divalent aromatic group, and n is an integer from 1 to 200.

14. A method of preparing an aromatic polyamide, substantially as hereinbefore described in any of Examples 1, 3 and 5.

15. An aromatic polyamide prepared by a method according to Claim 14.

16. A method of preparing a polybenzoxazole, substantially as hereinbefore described in any of Examples 2, 4, 6 and 7.

17. A polybenzoxazole prepared by a method according to Claim 16.